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Vibrational Spectra and Normal Vibrations of Tetracyanothiophene Anion Radicals

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Infrared spectra of tetracyanothiophene anion radicals were recorded at -78°C . Assignments of the observed bands to the individual fundamentals were carried out with the aid of the spectral data of the neutral molecule and the normal coordinate analysis. In this calculation, the modification of the force field was restricted to the stretching force constants, and the values of the bending and repulsion force constants were kept the same as the corresponding ones of the neutral molecule. The agreement between the observed and calculated frequencies was satisfactory. The values of the converged set of the stretching force constants suggest that the addition of an extra electron to the neutral molecule enhances the delocalization of the bonding electrons. This result was confirmed by the calculation of the bond population performed by the use of the CNDO/2 method.

KEY WORDS: Infrared spectra / Normal coordinate analysis / Tetracyano-
compound / Anion radical / Spectral change on ionization /
Electron distribution /

INTRODUCTION

Tetracyanothiophene (TCNT) which was first synthesized and physicochemically studied by Simmons and his co-workers¹⁾ is a conjugated tetracyano-compound containing a sulfur atom in the five-membered ring and is known as an electron acceptor in the charge-transfer complexes. Previously, infrared and Raman spectra of TCNT have been studied²⁾ by the present authors as a work in the series of vibrational studies of tetracyano-compounds.^{3~7)} Recently, infrared spectra of TCNT anion radicals (TCNT⁻) have been briefly reported.⁸⁾ The purpose of the present paper is to describe a detail of the infrared spectra and normal coordinate analysis of TCNT⁻. The difference of the spectra between TCNT and TCNT⁻ is interpreted as due to the change in the electron distribution. This result is confirmed by the calculation of the bond population performed by the use of the CNDO/2 method.

EXPERIMENTAL

The sample of TCNT is the same as that reported previously.²⁾ The TCNT⁻ sample was prepared by evaporating TCNT on the sodium film in the low-temperature infrared cell⁹⁾ shown in Fig. 1. The procedure of the preparation is as follows.

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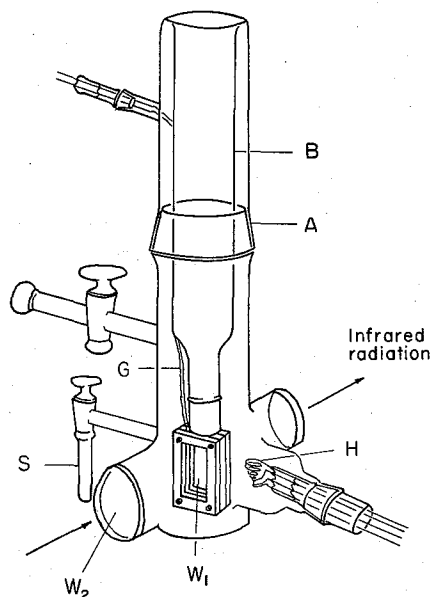


Fig. 1. Low-temperature cell for infrared measurements. A: Ground joint, B: Dewar, G: Thermocouple, H: Tungsten furnace, S: Sample container, W_1 : Inner window, W_2 : Outer window.

About 300 mg of the TCNT crystalline powder and 100 mg of the sodium metal were placed in the sample container S and the basket-formed tungsten furnace H, respectively. The cell was assembled so that the inner KBr window W_1 faced to the furnace and then connected to the vacuum system. After evacuation for several hours at 10^{-6} torr, the sodium metal was heated to 60°C for 30 minutes to remove a trace of volatile impurities. Then the inner KBr window was gradually cooled to -78°C by an introduction of dry-ice into acetone in the Dewar B. The temperature of the window was measured by a copper-constantan thermocouple G. The deposition of the sodium film on the window was carried out by heating the furnace to a temperature slightly lower than the melting point of sodium (98°C). Then, the inner window was turned by 180° with the aid of the ground joint A to be faced to the sample container S. TCNT was slowly heated up to about 100°C with a band heater and kept at this temperature while it was evaporated on the sodium film cooled to -78°C . The sample film was gradually colored in bluish dark brown, suggesting the formation of TCNT^- . After the inner window was turned by 90° to be parallel to the outer windows W_2 , the infrared spectra of the sample were recorded on a Perkin-Elmer model 521 spectrophotometer. A 10-cm gas cell was placed in the reference beam to compensate the atmospheric absorption and energy loss.

Figure 2 is the ESR spectrum of the sample prepared on the sodium film, lending an additional confirmation to the radical formation.

The infrared spectra of TCNT^- prepared on the various alkali halide films (LiI, NaI, KI, CsI, CsBr, and CsCl) were also recorded.

Vibrational Spectra of TCNT⁻

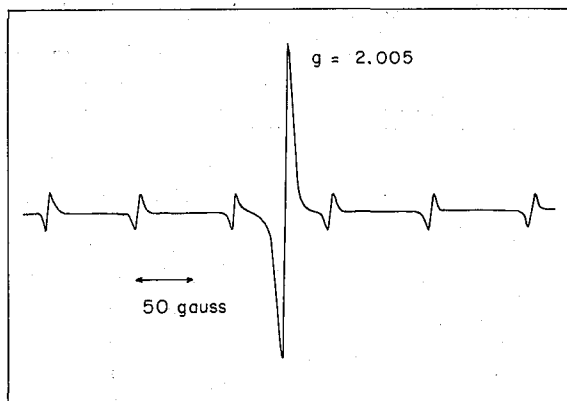


Fig. 2. ESR spectrum of TCNT⁻-Na⁺. Six weak absorptions are due to Mn²⁺ for calibration.

INFRARED SPECTRA OF TCNT⁻

Figure 3A is the infrared spectrum of the TCNT powder in the KBr pellet. Figures 3B and 3C are those of TCNT⁻ prepared at -78°C on the sodium metal and cesium chloride films, respectively. TCNT⁻ samples prepared on other alkali halide films gave similar spectra with Fig. 3C.

In Figs. 3B and 3C, the absorption bands marked with arrows are due to the neutral TCNT molecules remaining unreacted. A number of new bands appear on the conversion of the neutral molecule to the anion radicals. Although the relative

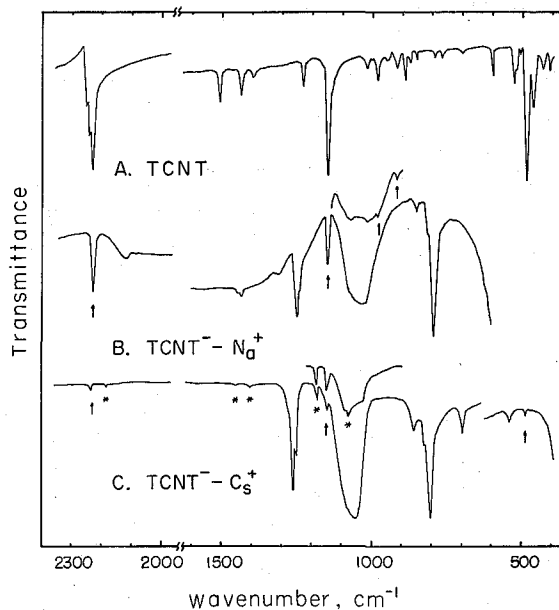


Fig. 3. Infrared spectra of (A) TCNT at a room temperature, and of (B) TCNT⁻-Na⁺ and (C) TCNT⁻-Cs⁺ at -78°C. Absorption bands marked with arrows and asterisks are due to neutral TCNT and impurities, respectively.

Table I. Infrared Spectra of TCNT and TCNT^{-a)}

TCNT ^{b)}		TCNT ⁻	
Frequency (cm ⁻¹)	Assignment ^{c)}	Frequency (cm ⁻¹)	Assignment ^{c)}
2258 w	ν_{13}	2120 ^{d)} w	ν_1
2247 w	ν_1		ν_2
2239 s	ν_{14}		ν_{13}
2224 w	ν_2		ν_{14}
1512 m	ν_{15}	1450 ^{d)} w	ν_{15}
1443 m	ν_3	1440 ^{d)} w	ν_3
1406 w	ν_4	1320 ^{d)} w	ν_4
1233 m	ν_{16}	1256 s	ν_{16}
1152 s	ν_5	1250 sh	ν_5
983 m	ν_{17}	1075 s, b	ν_{17}
896 m	ν_6	1025 s, b	ν_6
		855 w	
		820 sh	
770 w	ν_{18}	802 s	ν_{18}
		696 ^{e)} w	
530 m	ν_{19}	546 ^{e)} w	ν_7
524 sh	ν_7		ν_{19}

a) s: strong, m: medium, w: weak, sh: shoulder, b: broad.

b) KBr pellet.

c) Reference (2).

d) Observed only in the TCNT⁻-Na⁺ spectrum.e) Observed only in the TCNT⁻-Cs⁺ spectrum.

intensities of the new bands are different in Figs. 3B and 3C, the frequencies are almost the same in the both spectra. Thus these bands can be assigned to the TCNT⁻ vibrations. Unfortunately, the TCNT⁻ bands could not be observed in the frequency region lower than 700 cm⁻¹ in the TCNT⁻-Na⁺ spectrum and 400 cm⁻¹ in the TCNT⁻-Cs⁺ spectrum, because of an obstacle of a strong background. The infrared data of TCNT⁻ are summarized in Table I, together with those of TCNT.

ASSIGNMENTS

The assignments of the observed bands to the individual fundamentals were carried out with the aid of the spectral data of TCNT²⁾ and the normal coordinate analysis mentioned later. The comparison of the spectral data between TCNE and TCNE^{-10,11)} and that between TCNQ and TCNQ⁻¹²⁾ also furnished much information. The assignment could be accomplished without serious difficulties except for the ν_3 and ν_4 vibrations. The absorption bands attributable to these vibrations were found at 1440 and 1320 cm⁻¹. Since they were highly coupled modes of the C=C, C—C, and C—S stretching vibrations of the thiophene ring, the assignments were made with the aid of the normal coordinate analysis. Consequently, the band at 1440 cm⁻¹ was ascribed to the ν_3 vibration and that at 1320 cm⁻¹ to the ν_4 vibration. The results are listed in the last column of Table I.

Vibrational Spectra of TCNT⁻

It is seen in Table I that almost all the bands due to the stretching vibrations of the single bonds are shifted to the higher frequency side and those of the double and triple bonds to the lower frequency side in going from the neutral molecule to the anion radical. It is to be noted that the frequency shift of the C≡N stretching bands is very large (about -120 cm^{-1}) as compared with those for TCNE¹¹⁾ and TCNQ,¹²⁾ and is comparable with those for aromatic nitriles.¹³⁾

NORMAL COORDINATE ANALYSIS

The normal coordinate analysis of the in-plane fundamentals of TCNT⁻ was made by the GF matrix method¹⁴⁾ under the assumption of the C_{2v} point symmetry. The numerical calculations were carried out with a FACOM 230-48 digital computer of this institute. The internal coordinates of TCNT⁻ are given in Fig. 4. The molecular parameters were kept the same as for TCNT²⁾ owing to the lack of structural

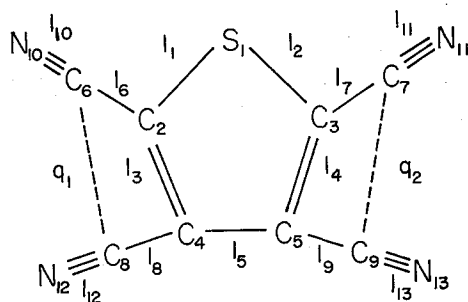


Fig. 4. Internal coordinates of TCNT⁻.

Table II. Force Constants (mdyn/Å)^{a)} and Bond Populations of TCNT and TCNT⁻

	Force constant			Bond population	
	TCNT	TCNT ^{-b)}		TCNT	TCNT ⁻
K (C—S)	4.15	4.82	C—S	1.802	1.808
K (C—C)	4.55	5.14	C—C (I) ^{e)}	1.754	1.774
			C—C (II) ^{e)}	1.742	1.749
K (C=C)	5.60	5.18	C=C	1.928	1.847
K (C—C, ring)	4.27	4.71	C—C (ring)	1.706	1.766
K (C≡N)	17.41	15.06	C≡N (I) ^{e)}	2.712	2.694
			C≡N (II) ^{e)}	2.719	2.709
$\alpha^c)$	0.41 ^{d)}	—			
β	—	0.60 ^{d)}			
γ	—	0.65 ^{d)}			

a) The relation $C' = -0.1C$ was assumed.

b) The values of the force constants H 's, F 's, and C were assumed to be the same as those of TCNT (see Text) and are not listed here.

c) The force constant α is the coefficient of the cross terms between the C=C and C—C stretching coordinates in the thiophene ring of TCNT.²⁾

d) Fixed.

e) The mark (I) refers to the C₂—C₆≡N₁₀ and C₃—C₇≡N₁₁ groups, and (II) to the C₄—C₈≡N₁₂ and C₅—C₉≡N₁₃ groups (see Fig. 4).

data for TCNT⁻ and considering the slight influence that a small variation of the geometrical parameters has on the calculated frequencies.

The modified Urey-Bradley force field $V(\text{mod. UBFF})$ given by

$$V(\text{mod. UBFF}) = V(\text{UBFF}) + \frac{1}{2} C \sum_{i=1}^2 (\Delta q_i)^2 + C' \sum_{i=1}^2 (\Delta q_i) q_i \\ + \beta (\Delta l_3 \Delta l_8 + \Delta l_4 \Delta l_9) + \gamma (\Delta l_5) (\Delta l_8 + \Delta l_9 - \Delta l_6 - \Delta l_7)$$

was used as the potential function of TCNT⁻. $V(\text{UBFF})$ consists of terms with five bond-stretching, seven angle-bending, and six non-bonded repulsion force constants.²⁰ The constant C is the coefficient of the *cis* non-bonded repulsion terms between two carbon atoms. The additional force constants β and γ were necessary to have a good

Table III. In-plane Fundamentals of TCNT⁻

	Obsd. freq. (cm ⁻¹)	Calcd. freq. (cm ⁻¹)	Dev. ^{a)} (%)	P.E.D. (%) ^{b),c)}
a ₁ ν_1	2120	2125	0.2	C≡N (I) str. (80)
ν_2	2120	2114	-0.3	C≡N (II) str. (81)
ν_3	1440	1449	0.6	C=C str. (49), C—C (ring) str. (28)
ν_4	1320	1326	0.5	C—C (ring) str. (20), C—S str. (20)
ν_5	1250	1228	-2.1	C—S str. (32), C—C (I) str. (30)
ν_6	1025	952	-7.1	C—C (II) str. (38)
ν_7	546	548	0.4	C—C (II) str. (29), C—S str. (25)
ν_8	—	463	—	C—C≡N (I) def. (30), $\begin{smallmatrix} \text{S} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (29)}$
ν_9	—	416	—	C—C≡N (II) def. (36), $\begin{smallmatrix} \text{C} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (25)}$
ν_{10}	—	327	—	C=C—S bend. (35), C—C (I) str. (22)
ν_{11}	—	124	—	C—C≡N (I) def. (53), $\begin{smallmatrix} \text{S} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (36)}$
ν_{12}	—	107	—	$\begin{smallmatrix} \text{C} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (47), C—C≡N (II) def. (36)}$
b ₂ ν_{13}	2120	2123	0.1	C≡N (I) str. (66)
ν_{14}	2120	2121	0.0	C≡N (II) str. (66)
ν_{15}	1450	1440	-0.7	C=C str. (60)
ν_{16}	1256	1277	1.7	C—S str. (29), C—C (I) str. (29)
ν_{17}	1075	1040	-3.3	C—C (II) str. (43), C—S str. (27)
ν_{18}	802	788	-1.7	$\begin{smallmatrix} \text{C} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (37), C—C (I) str. (31)}$
ν_{19}	546	545	-0.2	$\begin{smallmatrix} \text{S} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (36), C—S str. (32)}$
ν_{20}	—	453	—	C—C≡N (II) def. (29), $\begin{smallmatrix} \text{C} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (23)}$
ν_{21}	—	343	—	C=C—C bend. (37), C=C—S bend. (25)
ν_{22}	—	221	—	C—C≡N (I) def. (41), C—C≡N (II) def. (36)
ν_{23}	—	118	—	C—C≡N (I) def. (29), C—C≡N (II) def. (28)
				$\begin{smallmatrix} \text{C} \\ \diagdown \\ \text{C} \end{smallmatrix} \text{C} \text{—CN def. (22)}$

a) Dev. = $100 \{ \nu(\text{Calcd.}) - \nu(\text{Obsd.}) \} / \nu(\text{Obsd.})$

b) Only contributions greater than 20 per cent are included.

c) For the marks (I) and (II), see Table II.

agreement between the calculated and observed frequencies of the C=C and C—C stretching bands of the thiophene ring. The modification of the force field from that of TCNT was limited to the stretching force constants, because the ionization frequency shifts were mainly observed for the stretching vibration bands. The values of the bending and repulsion force constants were kept the same as the corresponding ones of TCNT.²⁾ After some refinements of the values by the trial-and-error method using the Jacobian matrix, repetitions of the calculation with several sets of the force constants were carried out by the least-squares method. The converged set of the force constants is shown in Table II, together with those of TCNT. In Table III, the frequencies calculated with these force constants are compared with the observed values. If one considers that only the stretching force constants were varied in the calculation, the agreement is satisfactory as far as the observed bands are concerned. The potential energy distribution is given in the last column of Table III.

It is apparent from Table II that the values of the single bond stretching force constants, $K(\text{C—S})$, $K(\text{C—C})$, and $K(\text{C—C, ring})$ of TCNT⁻ are larger than the corresponding values of TCNT, whereas those of the double and triple bond stretching force constants $K(\text{C=C})$ and $K(\text{C}\equiv\text{N})$ of TCNT⁻ are smaller. Consequently, the values of the single bond stretching force constants become comparable with that of $K(\text{C=C})$. Thus it can be concluded that the addition of an extra electron to the neutral molecule causes an enhancement of the delocalization of the bonding electrons. The introduction of the force constants β and γ may make less significant the information about the potential function, however, it does not affect the trend of changes in the values of the stretching force constants on ionization of TCNT.

The lack of observed frequencies of the deformation vibrations does not allow us further discussions to rationalize the ionization frequency shifts.

BOND POPULATION

In order to confirm the above conclusion about the electron distribution, the bond population of the electrons was calculated for TCNT and TCNT⁻ using the CNDO/2 method developed by Pople.¹⁵⁾ The results are also listed in Table II. Although, the differences of the bond populations between TCNT and TCNT⁻ are small, the trend of the changes in the bond populations on ionization is consistent with that of the changes in the force constants.

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